



Determination of Diesel Range Organics (DROs) Using SPE and GC/FID by Method 8015D*

UCT Products:

ECUNIPAH (ENVIRO-CLEAN® Universal PAH/DRO 2000 mg/83 mL cartridge)

Method Summary

Method 8015D may be used to determine the concentrations of several nonhalogenated volatile organic compounds and semivolatile organic compounds using GC with flame ionization detection. This application outlines a solid phase extraction method using C18 to determine DROs in water sample matrices.

- Diesel Range Organics (**DRO**) corresponds to the range of alkanes from C₁₀ to C₂₈ and covering a boiling point range of approximately 170° C - 430° C

Sample Collection, Preservation, and Storage

- See sample collection options EPA Method 5035A

Interferences

- Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis
- All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks
- Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary
- Contamination by carryover occurs whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be rinsed out between samples with an appropriate solvent
- All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water
- Drain the glassware and dry it in an oven (except volumetric glassware) at 130° C for several hours or rinse it with methanol

- FID is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis and potential for analytes to be resolved poorly, especially in samples that contain many analytes.

Reagents and Standards

- Reagent grade chemicals must be used in all tests
- Organic-free reagent water
- Methanol, CH₃OH - Pesticide quality or equivalent
- Methylene Chloride – Pesticide residue quality or equivalent
- Fuels, e.g., diesel - Purchase from a commercial source
- Alkane standard - Standard contains a homologous series of *n*-alkanes for establishing retention times (e.g., C₁₀-C₂₈ for diesel)

Stock Standards

- Prepared from pure standard materials or purchased as certified solution
- Standards must be replaced after 6 months

Secondary Dilution Standards

- Using stock standard solutions, prepare secondary dilution standards in methanol, as needed either singly or mixed together
- Secondary dilution standards should be stored with minimal headspace for volatiles
- Check frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards

Recommended GC Columns

The choice of GC column will depend on the analytes of interest, expected concentrations, and intended use of the results. The capillary columns are necessary for petroleum hydrocarbon analyses and are recommended for all other analyses. Other columns and may be employed if the analyst can demonstrate acceptable performance.

- Establish the GC operating conditions appropriate for the GC column being utilized and the target analytes specified in the project plan
- Optimize the instrumental conditions for resolution of the target analytes and sensitivity
- Suggested operating conditions and GC programs are given below for the recommend columns:

(DRO) 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 5% methyl silicone (DB-5, SPB-5, RTX-5, or equivalent), 1.5- μ m film thickness

- Carrier gas (He) flow rate: 5-7 mL/min
- Makeup gas (He) flow rate: 30 mL/min
- Injector temperature: 200° C
- Detector temperature: 340° C
- Temperature program: Initial temperature: 45° C, hold for 3 minutes
- Program: 45° C to 275° C, at 12° C/min
- Final temperature: 275° C, hold for 12 minutes

SPE Procedure**

1. Condition Cartridge

- a) Assemble an SPE manifold system **UCT ECUCTVAC1, ECUCTVAC3 or ECUCTVAC6** (1,3 or 6 station)
- b) Place a **ECUNIPAH** cartridge(s) on the vacuum manifold
- c) With vacuum off add 10 mL of methylene chloride to the cartridge
- d) Let it soak for 1 minute
- e) Turn on vacuum and draw through to waste
- f) Draw vacuum through the cartridge to remove all methylene chloride
- g) Add 10 mL of methanol to the cartridge
- h) Draw the methanol to the level of the frit
- i) Add 10 mL of deionized water to the cartridge
- j) Draw most of the water to waste but do not allow the sorbent to dry

Note: Do not let the cartridge go completely dry after addition of methanol otherwise repeat starting at step 1.g)

2. Sample Addition

- a) Adjust the pH of the sample to 2 or less using 5 mL of 1:1 HCl, shake
- b) Add surrogate, and DRO spiking solution for fortified samples, to 1 mL methanol in a test tube, then transfer the mix to the water sample. Rinse the test tube with 1 mL methanol, transfer the rinse to the sample, and mix well. This helps to improve the recovery of LCS samples, especially for the lightweight hydrocarbons.
- c) Add the sample to the cartridge under vacuum. Draw the sample through the cartridge no faster than 20 – 30 minutes per liter
- d) Allow the cartridge to dry under full vacuum for 5 minutes***

3. Extract Elution

- a) Place a collection tube or vial in the vacuum manifold, and add approximately 1 cm of pre-baked sodium sulfate anhydrous to the SPE cartridge
- b) Rinse sample bottle with 10 mL of methylene chloride to remove any analyte from the glass
- c) Add the methylene chloride rinse to the cartridge
- d) Allow to soak for 1-2 minutes then draw through
- e) Repeat this procedure three more times using 10 mL aliquots of methylene chloride
- f) Dry the extract by passing it through about 10-20 grams of methylene chloride pre-rinsed sodium sulfate **ECSS25K**
- g) Thoroughly rinse the collection container with methylene chloride and add this solvent to the sodium sulfate and collect

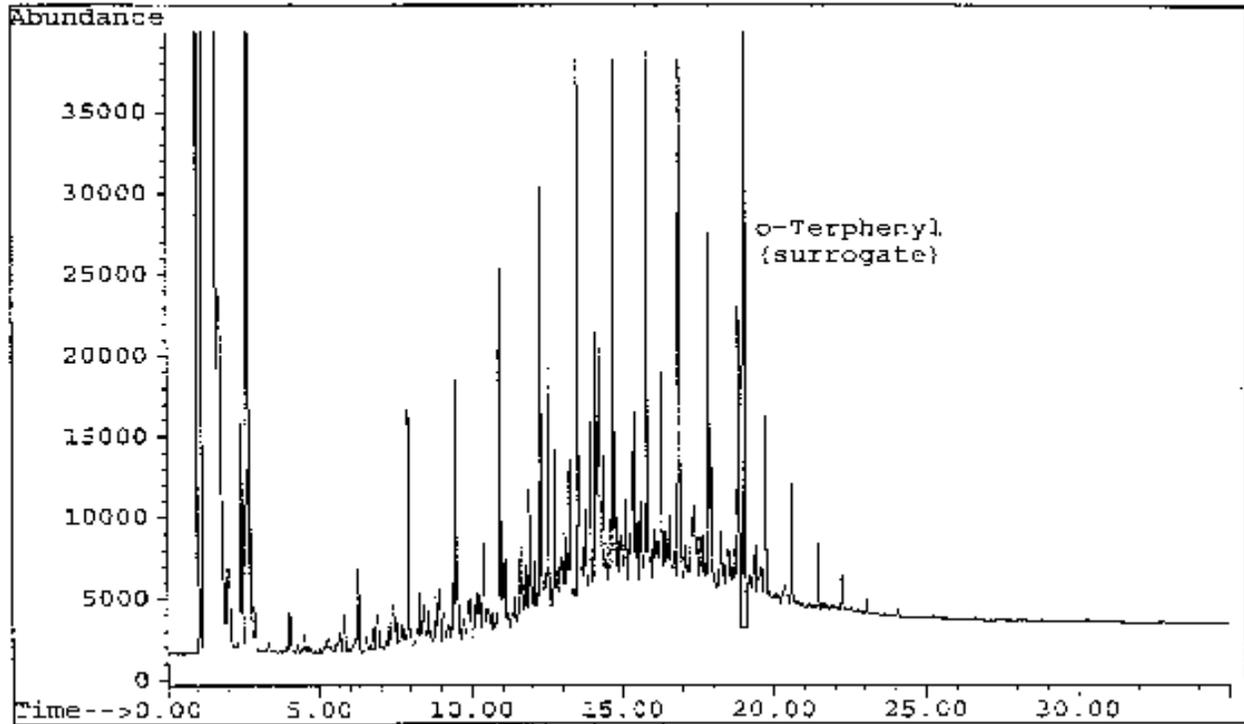
4. Concentration

Option 1: Evaporate the dried extract to 1 mL using Turbovap with a gentle stream of nitrogen (7-8 psi) at 35 °C. Do not overdry the extract otherwise low recovery will result due to the loss of more volatile hydrocarbons.

Option 2: Concentration of final extract using a micro Kaderna-Danish flask equipped with a 3-ball Snyder column is recommended to avoid loss of low boiling alkanes. A micro-Snyder column can be used to evaporate the extract to a 1 mL final volume.

Note: Extracts should not be stored with headspace for extended periods of time as low recoveries will result

Example Chromatogram of a 30 ppm Diesel Standard



Accuracy and Precision of LCS (Spiked at 500 ppm)

Analyte	Ave Recovery%	RSD% (n=3)
Diesel	100.7	1.5

*Summarized from Method 8015D Nonhalogenated Organics Using GC/FID, Revision 4, June 2003, and associated appropriate methods

** (steps 1- 4 added to this method summary for use with UCT PAH/DRO cartridges)

***Faster drying results can be obtained by removing the cartridge during drying and shaking or tapping the excess moisture from the bottom of the cartridge. Drying times are approximate. Do not over dry as low recoveries may result

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